DoD EPA DOE SERDP
Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

Electroformed Nanocrystalline Coatings An Advanced Alternative to Hard-Chrome Electroplating PP-1152

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Report Documentation Page

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Technical Objective

- **Develop an environmentally benign advanced nanocrystalline Co-based coating technology that:**
  - **Is compatible with conventional electroplating infrastructure**
  - **Will produce coatings that meet or exceed the overall performance of hard chrome (hardness, wear, fatigue, corrosion, and thermal stability)**
  - **Has costs similar to or less than life-cycle cost of existing hard chrome electroplating processes**
  - **Will be applied to non-line-of-sight surfaces**
- **Cobalt alloy selection**
  - **Mechanical properties**
  - **High plating efficiency**
  - **No constituents on EPA or AFMC lists of hazardous materials**
  - **Longer term view**

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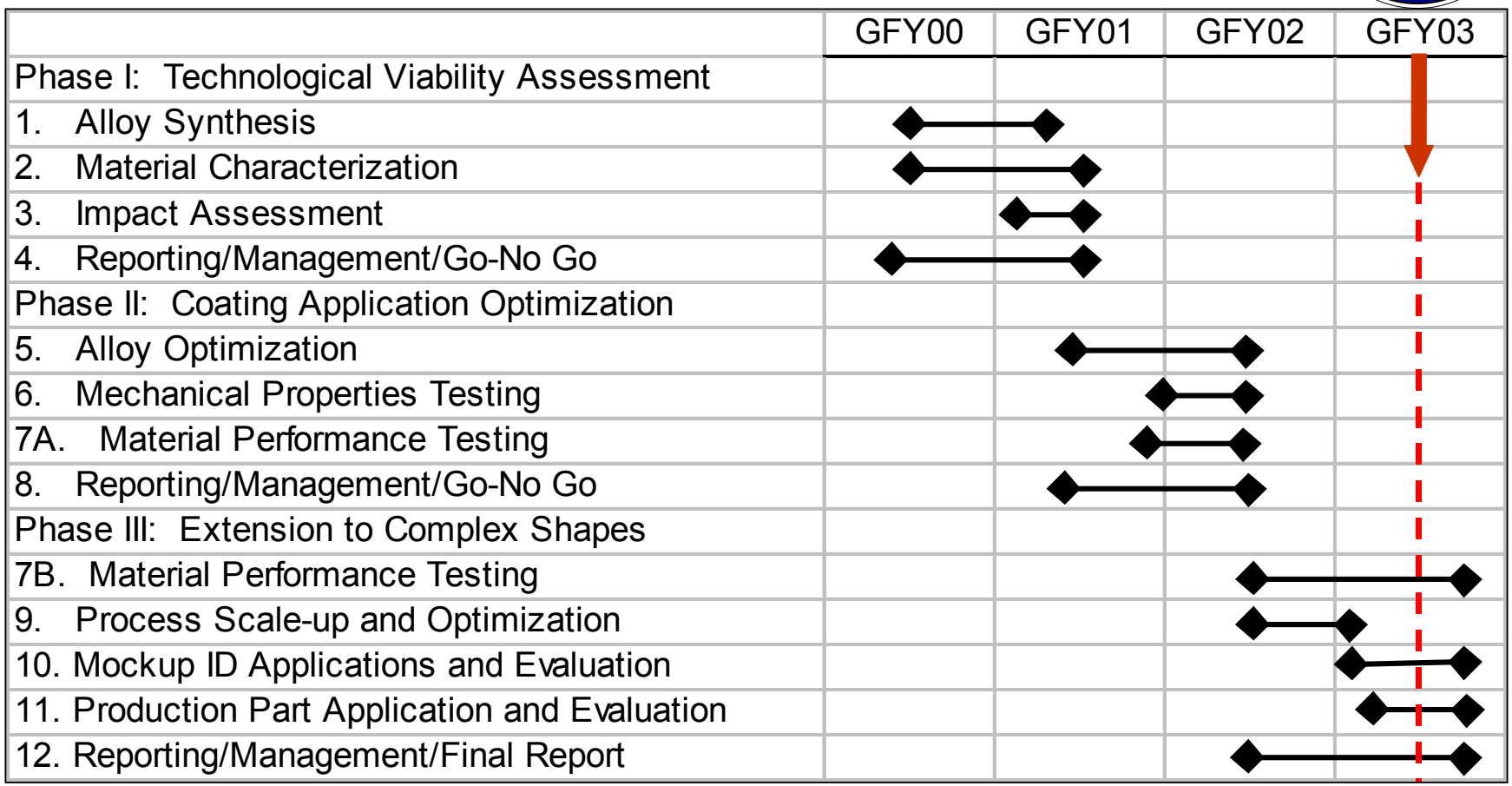
Program Overview

Three Phases

- **Phase I Technology Viability Assessment**
  - Completed
- **Phase II Coating Optimization**
  - Completed
- **Phase III Extension to Complex ID Shapes**
  - In Progress

Program Plan



Background

- Synthesized Co-P, Co-Mo and Co-Fe nano alloys
- Synthesized and Optimized Co-Fe,Co-Fe-P, Co-Fe-Zn and Co-Fe-Zn-P nano alloys
- Optimized Co-P alloy
  - Cobalt chloride/ortho-phosphoric/phosphorous acid bath
  - Plating efficiency >90%
  - Grain size 12-15 nm
  - As-deposited hardness 700 VHN
  - Deposition rate 2-8 mills/hr
  - Precipitation hardenable
  - Good salt spray results
  - High Taber wear results (CS 17)
  - Good pin-on-disk results

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Activities Since Toronto

- Initial fatigue tests completed
- Initial hydrogen embrittlement tests completed
- Electrochemical tests completed
- Stripping study completed
- Representative ID geometry plated

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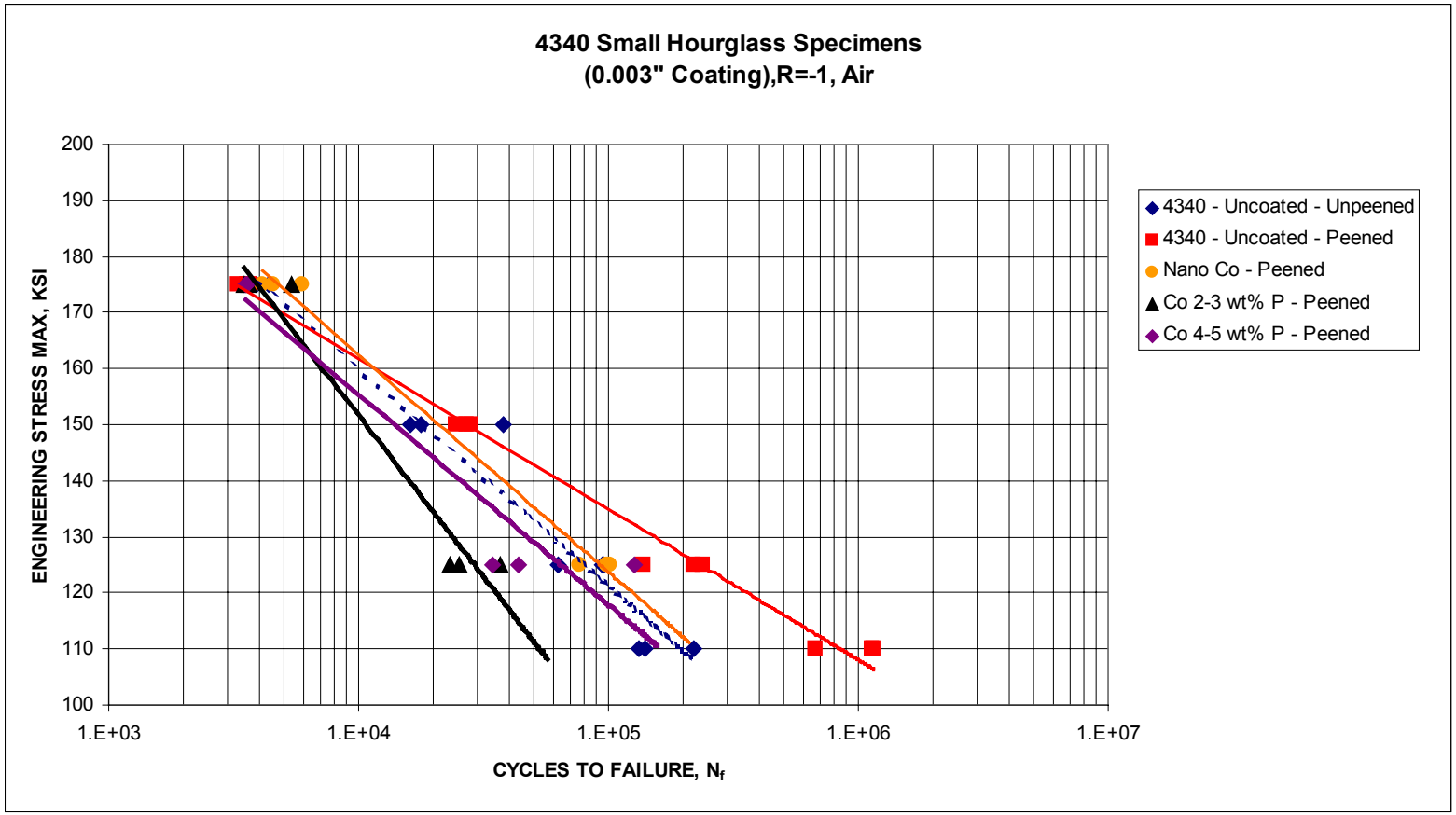
Initial Fatigue Test Matrix

- **4340 HT (avg. ~46 Rc)**
- **R= -1, Air**

Coating	Grit Blast	Peen	Final Ground Thickness (in)	No. Specimens
Bare	No	No	N/A	12*
Bare	No	Yes	N/A	12*
Nano Co 2-3% P	Yes	Yes	0.003	6+
Nano Co 4-5% P	Yes	Yes	0.003	6+
Nano Co	Yes	Yes	0.003	6+

* ksi/Hz 175 (5), 150 (5), 125 (10), 110 (10)
+ ksi/Hz 175 (5), 125 (10)

Fatigue Test Results



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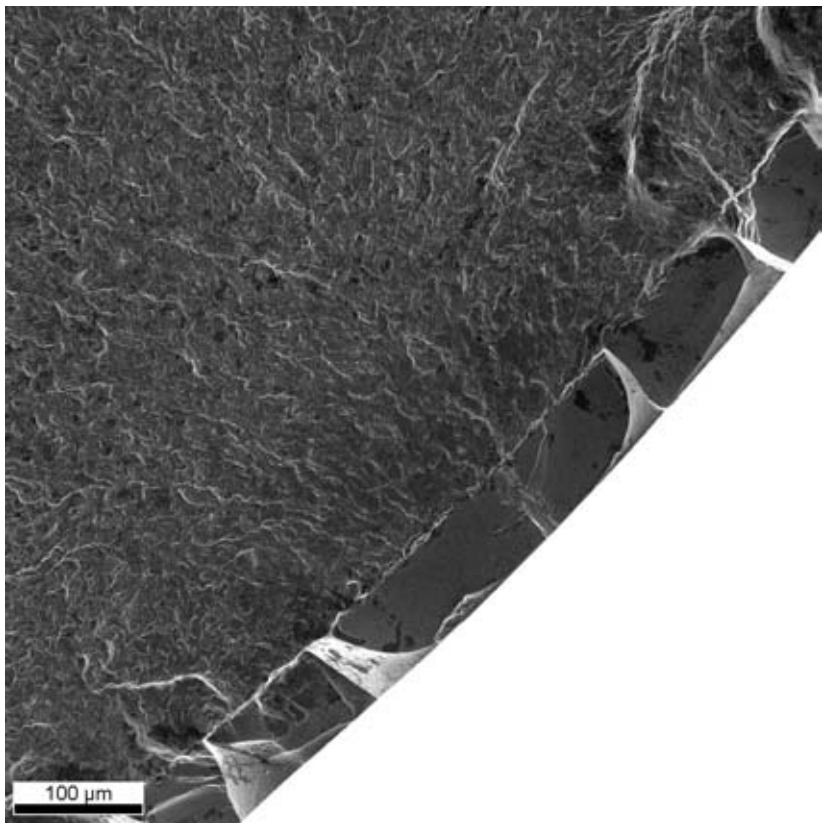
Fatigue Test Observations

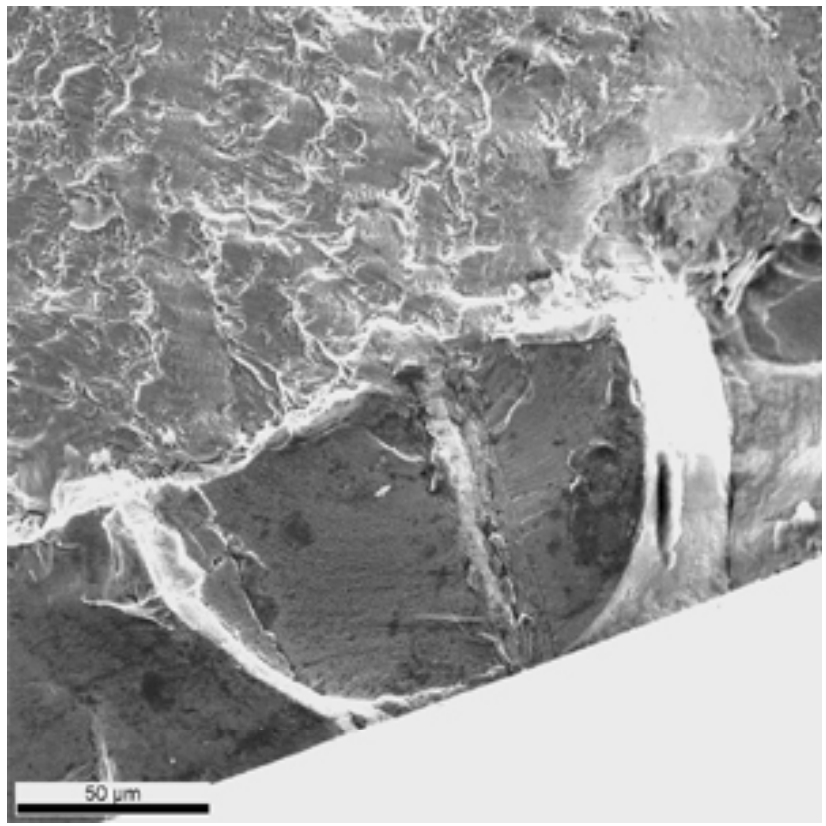
- **Specimens were significantly softer than JTP criteria**
  - **Cannot compare with HCAT EHC results**
- **Debit evident for Co-P alloys**
  - **Failures initiate at coating to substrate interface**
  - **Does not appear to be adhesion problem**
- **Retest**
  - **Ensure Specimens meet hardness criteria**
  - **Include EHC specimens in retest matrix**
  - **Evaluate effect of reducing internal stress**

Fatigue Results

2-3wt% P



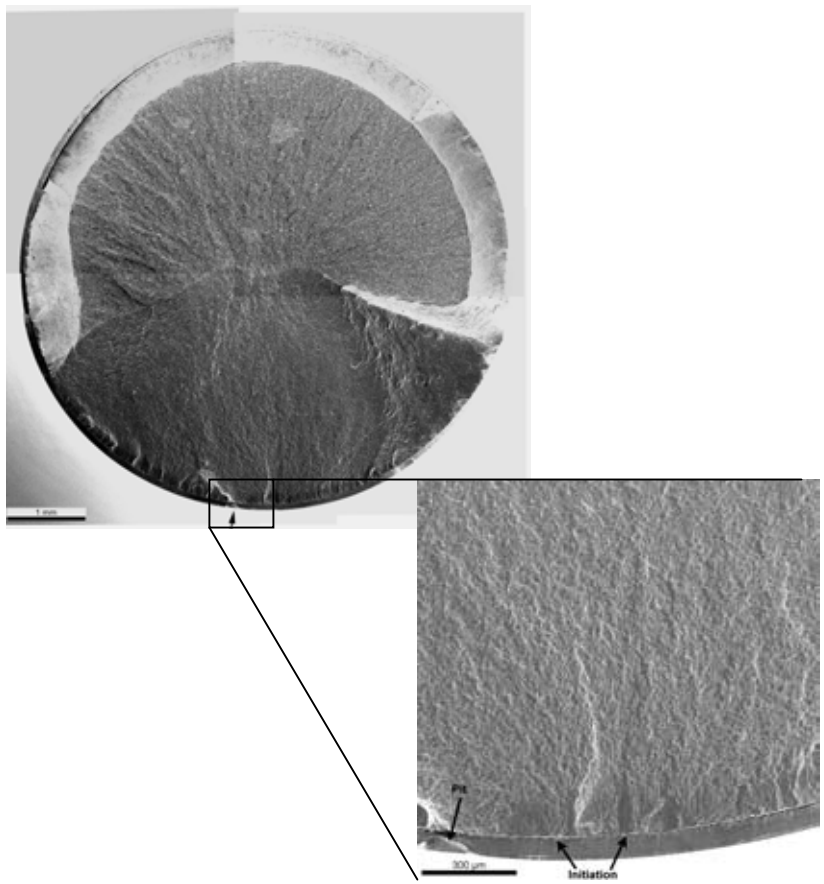
125ksi



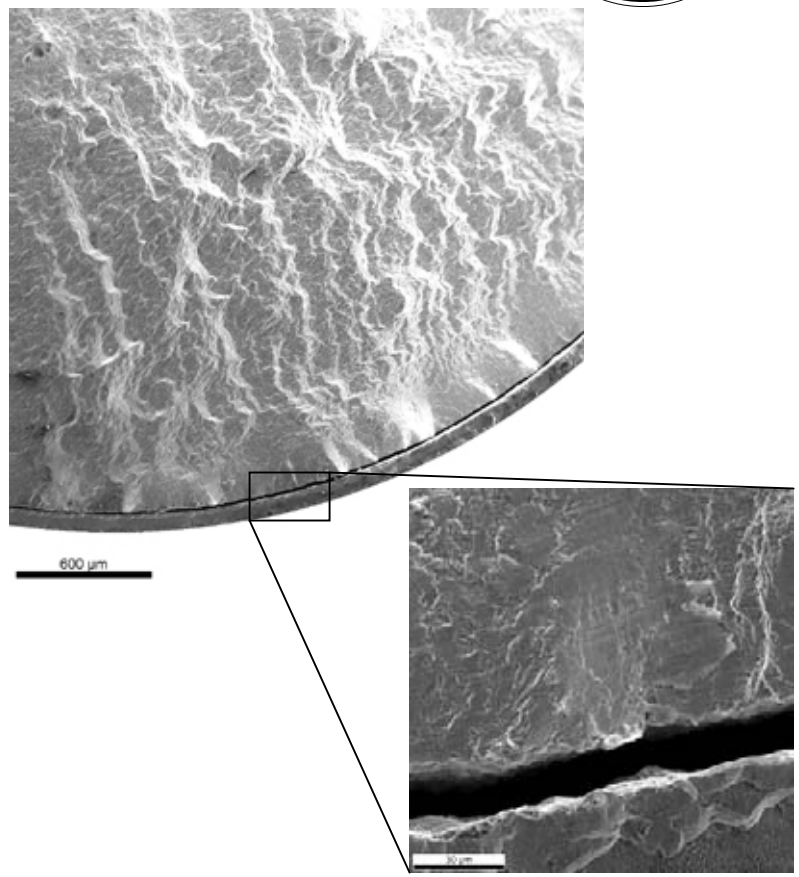
175ksi

Fatigue Results

4-5wt% P



125ksi



175ksi

Initial H_2 Embrittlement Test

- ASTM Type 1a Specimens -.003" coating thickness
- Acceptance criteria: 4 > 200 hrs @ 75% NFS or 3 > 90% NFS for 1 hr
- Notch failure except as indicated

	Hours (NFS)		
Coating Composition	No Bake	191 °C/ 12 hours	191 °C/ 12 hours
Bare	10 for NFS	-	-
Nano Co 2-3 wt%P	150 (75) 215 (83) 239 (82) 200 (80)	110 (75) BHF 162 (75) BHF 110 (75) BHF 215 (84)	180 (75) 233 (80) 233 (78) 233 (80)
Nano Co 4-5 wt%P	-	<18 (75) <18 (75) <64 (75) <64 (75)	216 (84) 216 (84) 216 (82) <46 (75)

BHF = Button Head Failure

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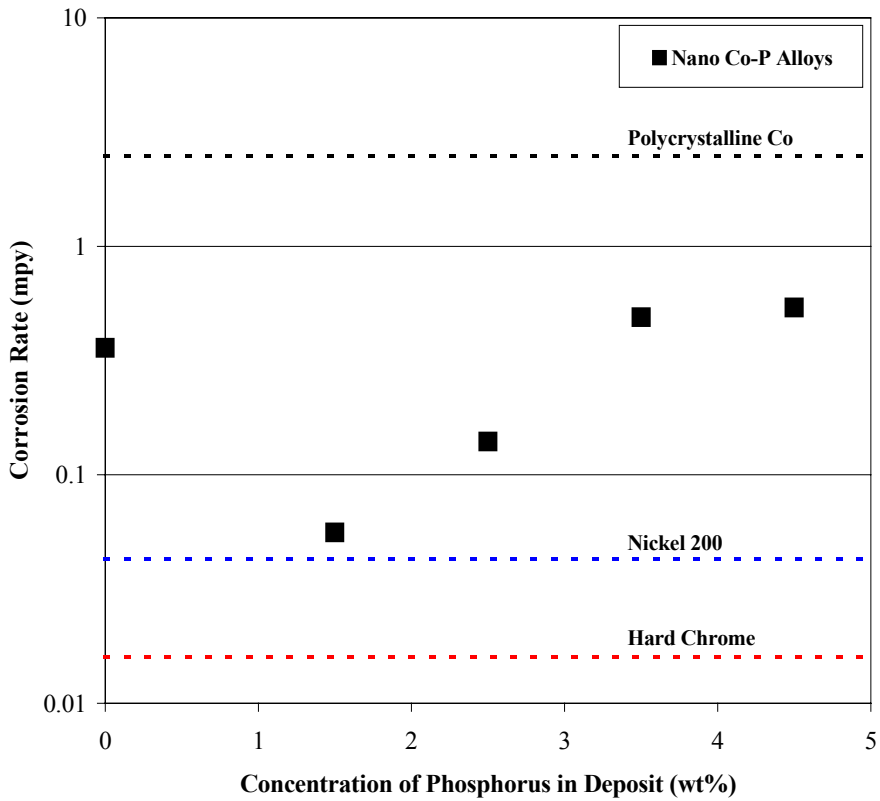
H_2 Embrittlement Retest

- Nano Co 2-3 wt% P
- Careful NDE of test specimens before plating
- Bake at 8 and 16 hours
- Include stripped, re-coated and baked specimens

Electrochemical Testing

- Linear polarization resistance scan (LRP) per ASTM G61
- 3.56 wt% NaCl, room temperature



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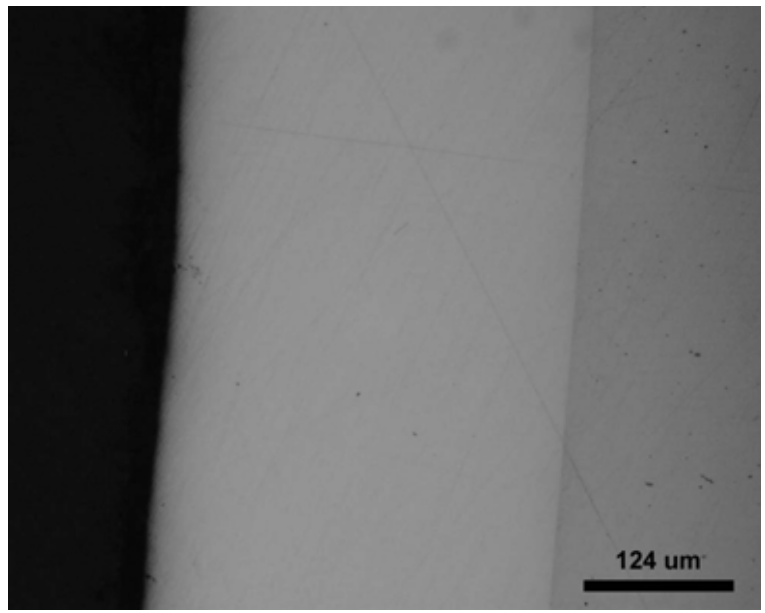
Chemical Stripping

- 4130 substrate - .005” Co 2-3 wt%P coating
- Evaluated HVOF Rochelle salt solution with anodic polarization
  - Low removal rate (<1gm/hr) at pH ~10
  - Faster removal rate (2-3 gm/hr) at higher carbonate concentration - substrate pitting noted
- Evaluated concentrated nitric acid
  - Fast removal rate (4-8 gm/hr)
  - Little substrate impact (.13% weight loss after 20 hour immersion)

Application to ID Surfaces

- **Mockups utilized**
  - **Blind and through cylinders**
  - **Pins**
  - **External lugs**
- **Anode design study**
  - **Small ID surfaces**
    - **Non-consumable graphite anode**
  - **Large ID surfaces**
    - **Consumable Co anode**



Optical Micrograph - 13 mil Nano Co 2-3wt%P coating on 1" ID

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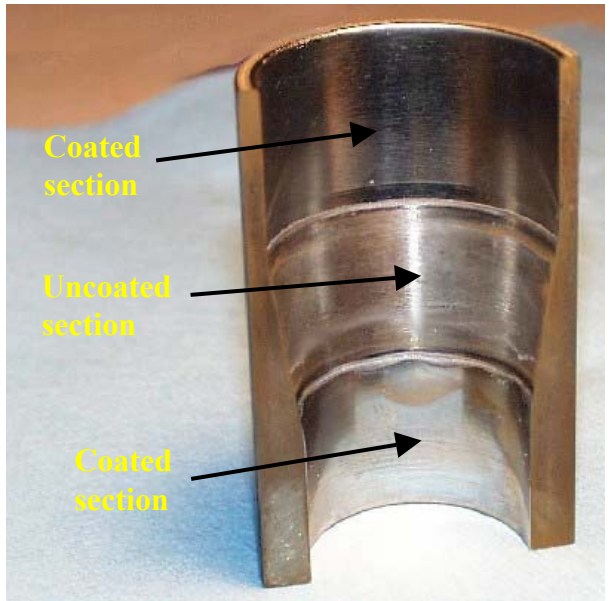
Small ID Surfaces

Stepped ID



- Stepped graphite anode
- Plastic plug used to mask uncoated section, with holes to allow for flow

- Uniform coating thickness on the two ID surfaces

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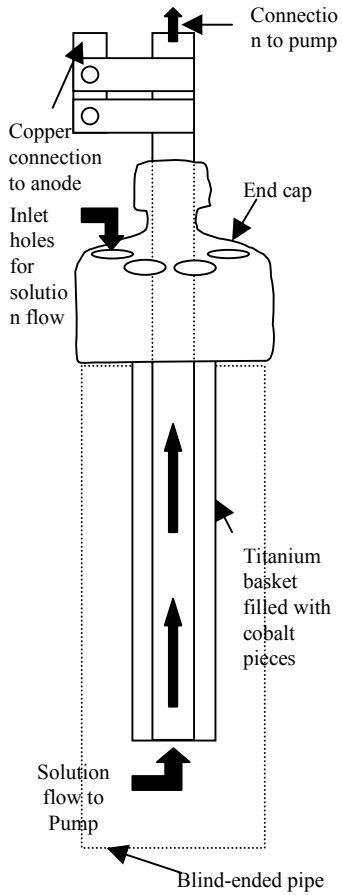
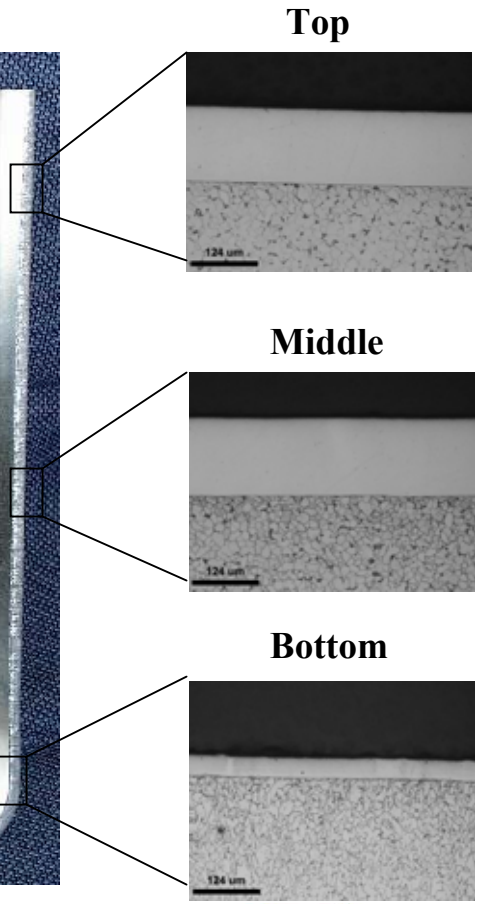
Large ID Blind Hole

Plating Assembly





Process Data Summary

	Nanocrystalline Co-P Alloy	Hard Chrome
Bath Chemsitry	Co 2-5wt%P ($CoCl_2$ / H_3PO_4 / H_3PO_3)	Cr (CrO_3 / SO_4^{2-})
Efficiency	85-95%	15-35%
Deposition Rate	Up to 8 mil per hour	Up to 1.6 mil per hour
Thickness	Demonstrated up to 0.020”	Typically < .005”
As-Deposited Appearance	Pit / Pore Free	Microcracked
Microstructure	Nanocrystalline (avg. g.s. = 8 -15nm)	-
Relative Process Cost	1.3	1.0
Emission Analysis	Below OSHA limits	Cr^{6+}

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Property Data Summary

		Nanocrystalline Co-P	Hard Chrome
Hardness	*As-Deposited*	600-700 VHN	800-1200 VHN
	HT @ 250°C	700-800 VHN	-
	HT @ 400°C	1000-1200 VHN	-
Ductility		2 – 7 % Elongation	<.1%
Thermal Stability		400°C	-
Wear	*Abrasive (Taber)*	27 mg / 1000 cycles (CS-17) 11 mg / 1000 cycles (CS-10)	3.2 mg / 1000 cycles (CS-17) 1.0 mg / 1000 cycles (CS-10)
	Adhesive (Pin-on-disk)	5-6 x 10^{-6} mm^3/Nm (Alumina Ball on Nano Co-P Disk)	9-11 x 10^{-6} mm^3/Nm (Alumina Ball on Cr Disk)
	Coefficient of Friction	0.5	0.7
Corrosion	Salt Spray	Protection Rating 7 @ 1000 hrs	Protection Rating 2 @ 1000 hrs
	Poteniodynamic	.07 - .15 mpy	.02 mpy
Internal Stress		10-15 ksi (Tensile)	Cracked – Exceeds cohesive strength
Hydrogen Embrittlement		Additional tests planned	Yes – min bake 14 hrs
Fatigue		Additional tests planned	Fatigue Debit

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Remaining Actions

- Conduct final material tests
- Complete ID application demonstrations
- Submit final report
- Submit ESTCP white paper proposal